

A Direct-push-based, Geochemical Assessment of Natural Attenuation at a Former Underground Storage Tank Site

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-In the 1990's the Wisc. DNR and Dept of Commerce initiated closure procedures for 10 underground storage tank sites. Although contaminated groundwater was present at the time of closure for many of these sites, their removal from monitoring programs was accepted based on the assumption that small amounts of contaminants remaining would be reduced over time by natural remedial processes.

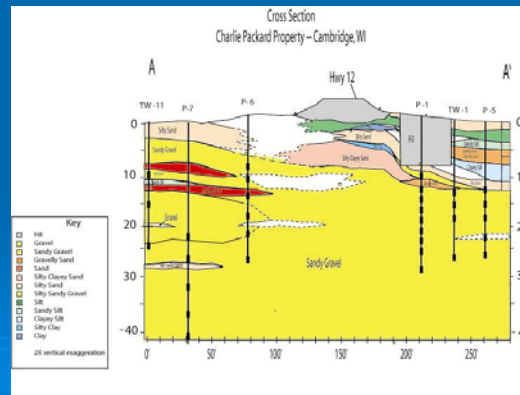
-The work that I will present today is part of a post-closure review process in which several of these sites are being evaluated.

Introduction

- Decisions to discontinue monitoring programs at contaminated underground storage tank sites are often based on assumptions of natural attenuation.
- Natural attenuation can be difficult to assess in heterogeneous aquifers, where sharp chemical gradients can occur or temporal variations in ground-water flow conditions exist.
- A high-resolution sampling approach can allow for accurate assessment of chemical heterogeneity, and enable identification of zones of natural attenuation.
- A detailed assessment of a former LUST site was conducted using a new high-resolution, direct-push geochemical profiling method.

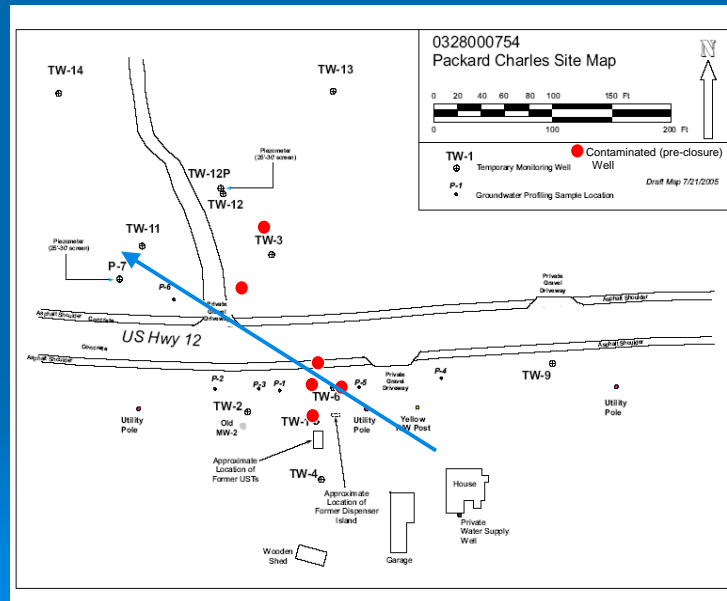
- Given the heterogeneity that exists in natural aquifer media, processes of chemical reduction can exist in localized zones.
- This makes screening for the occurrence of natural degradation processes difficult, especially when monitoring is conducted in wells with fixed locations.
- To enable flexibility in the detection of natural attenuation processes, a new direct-push geochemical profiling approach was used to for interactive field screening of natural attenuation processes.
- This presentation is a sequel to the last talk and represents a first application of the new method in contaminated groundwater

Site Conditions and Geology



- The LUST site examined is located on a strip of land between two lakes.
- The Site was closed in 2001 after excavation to depth of 10 ft. the source area and roughly 10 years of monitoring.
- In this view toward the east, the wetland/marsh/lake area can be seen in the south on the right side of the photo.
- The site is underlain by glacial sediments. Fine-grained materials (Silt, sandy silt and clay) are present in the upper 20 feet and grade laterally into sandy gravels to the east
- Below 20 ft, the aquifer consists primarily of coarse gravel
- Fine sands and silts beneath site are replaced with coarser materials near the surface at the north end of the site.
- One important features is the highway in the foreground. This road was replaced within the last few years and storm-water runoff system was modified. Runoff collects in the drainage ditch along the north side of the road and is diverted to the adjacent wetland.

Historic Contamination and Current Flow Direction



- BTEX compounds and naphthalene were observed in wells immediately adjacent to the tank basin with benzene concentrations as high as 20,000 $\mu\text{g/L}$.

- Groundwater flow direction was toward the NW.

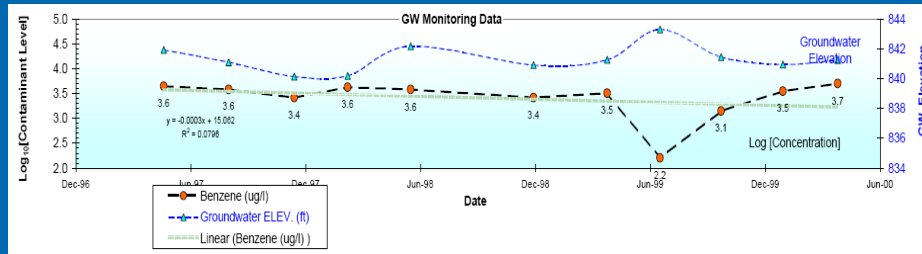
- Btex was observed in two well north of the highway in early monitoring but was not observed for a year prior to site closure

- Low levels of Napthalene were also observed and were present below enforcement levels north of the highway at the time of closure 10 years of monitoring.

- Although high levels of some constituents remained upon closure, the plume the assumption that the contaminant plume was being controlled by natural attenuation and would remain stable or shrink.

- In a recent evalution, the ground-water flow is toward the NW with a gradient of 0.001. The flow direction is believed to have shifted since the initial monitoring was conducted, possibly as a result response to road construction modifications

Historic Benzene Concentrations near Source Area



- A recent DNR analysis of several contaminants revealed that contaminant concentrations during the monitoring period remained relatively constant.
- In this example, fluctuations in benzene concentrations appear to be associated with changes in water levels.
- The persistence of benzene suggests that the source area may not have been completely excavated and that contaminated soil continues to impact groundwater.
- This investigation examined the role of natural attenuation in maintaining the contaminant plume

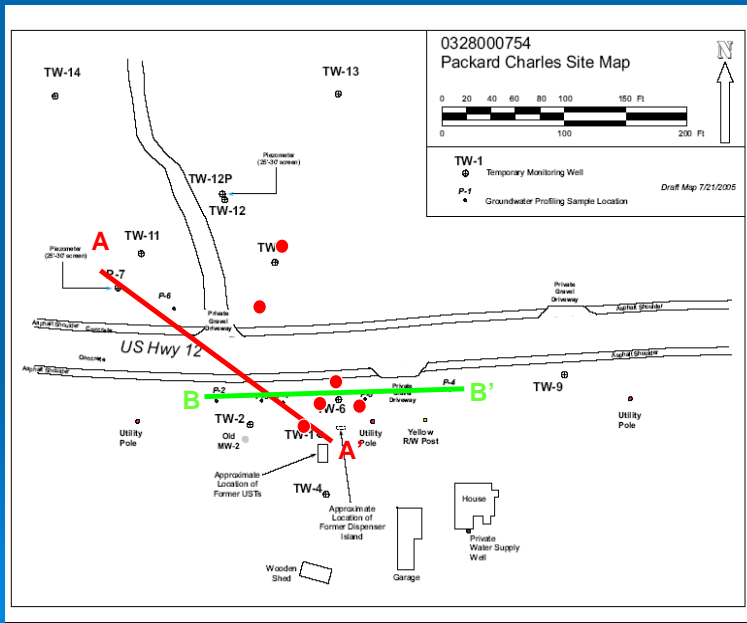
Sampling and Analytical Methods

- Direct-push geochemical profiler and mechanical bladder pump
- Samples obtained for field and laboratory analysis of inorganic and organic constituents at discrete depths
- Field analytical tools
 - Field Spectrophotometer
 - Multi-parameter sonde



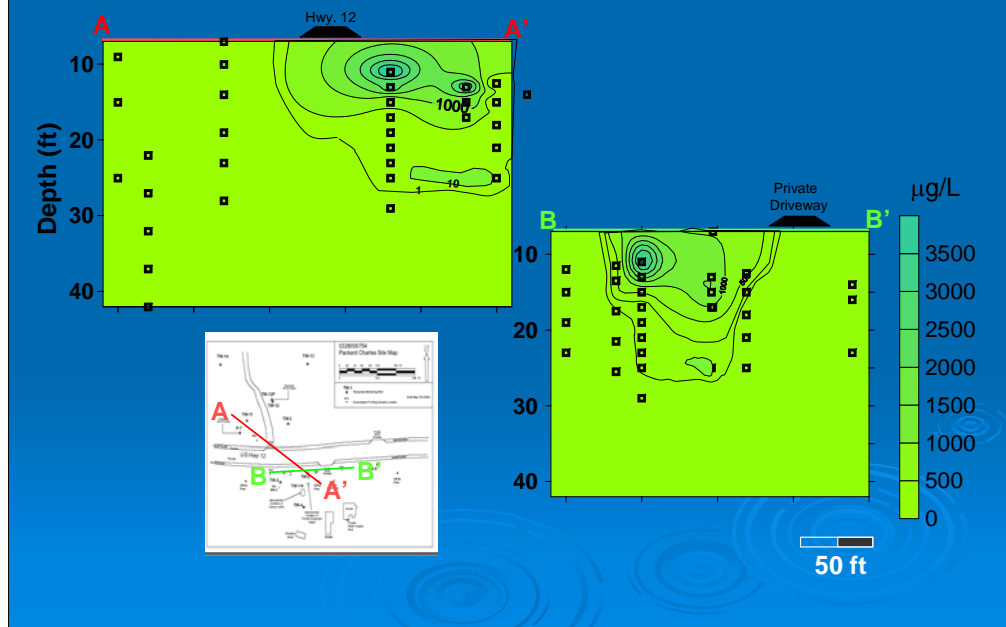
- To identify natural attenuation processes, high-resolution sampling was conducted using the new direct-push based approach described in the last talk.
- Discrete-depth samples were obtained using a 12-inch, stainless steel screened sampler at multiple depths in a single probe hole
- A Mechanical bladder pump was used to obtain the samples
- DO, Fe+2, Mn, and SO4 concentrations were measured in the field prior to the collection of samples for additional lab analysis of organic contaminants.

Sampling Transects



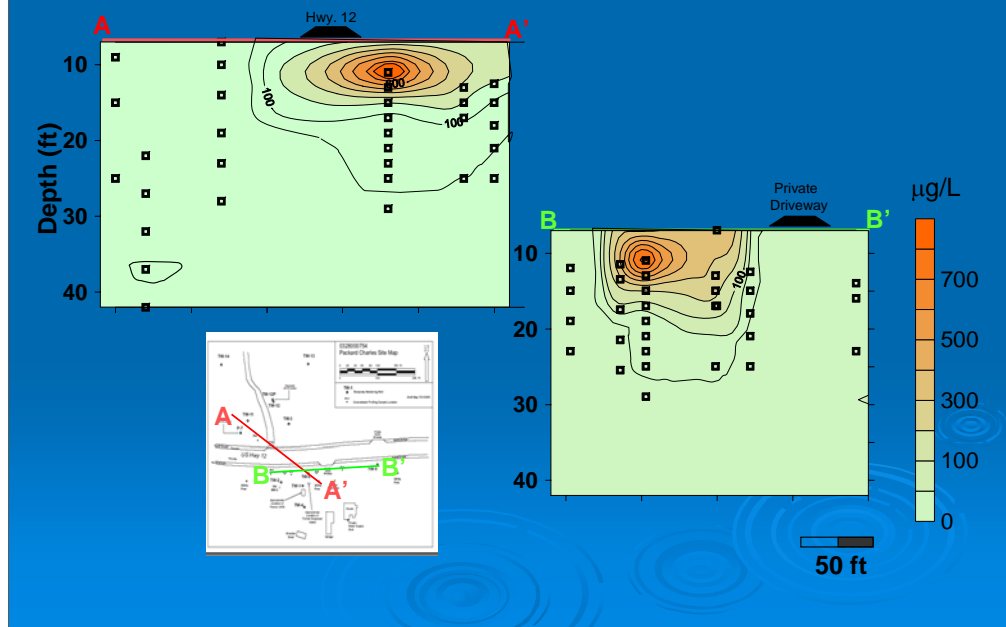
- Samples were collected from xx depths in xx probe locations along two transects across the site over a 4-day period
- Sampling locations and depths were determined in the field, based on the presence of natural attenuation parameters and qualitative field screening for volatile organic compounds.
- Sampling depths range from the top of the water table (7 ft) where possible to 42 ft.
- Additional data obtained from wells were included in this analysis

Benzene



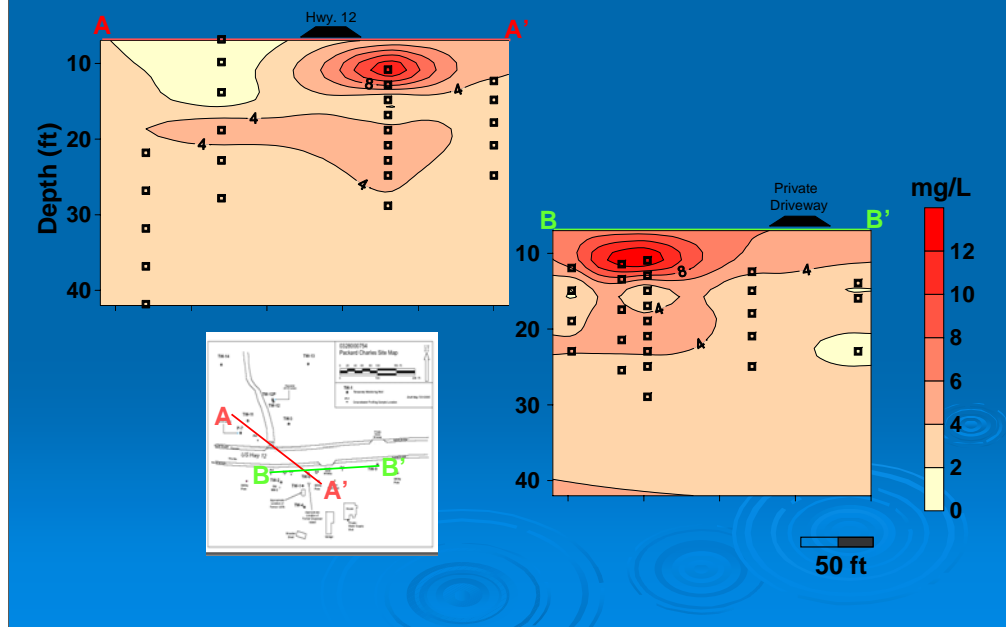
- BTEX contaminants were only found in the vicinity of the source area.
- Benzene is not observed below 29 feet depth and was not noted north of the road
- Although time-series trends suggest that contaminant levels in the source area are not dropping, the BTEX plume does not appear to have moved beyond it's position at the time of site closure.

Napthalene



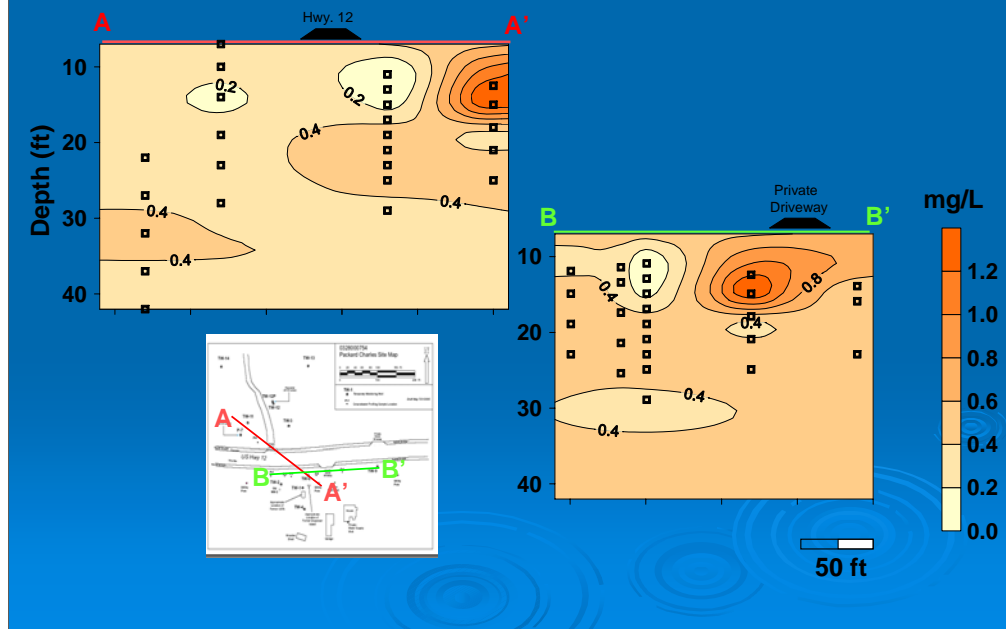
- Napthalene is also present near the source area and also is observed at depths of 29 ft.
- It was also observed in one sampling depth north of the highway.
- Napthalene was previously observed in similar concentrations but at shallower depths and further east on the north side of the highway. Its presence during this investigation suggest that napthalene is not maintained near the source
- Its presence west of the original location may be in agreement with a changing flow direction.

Ferrous Iron



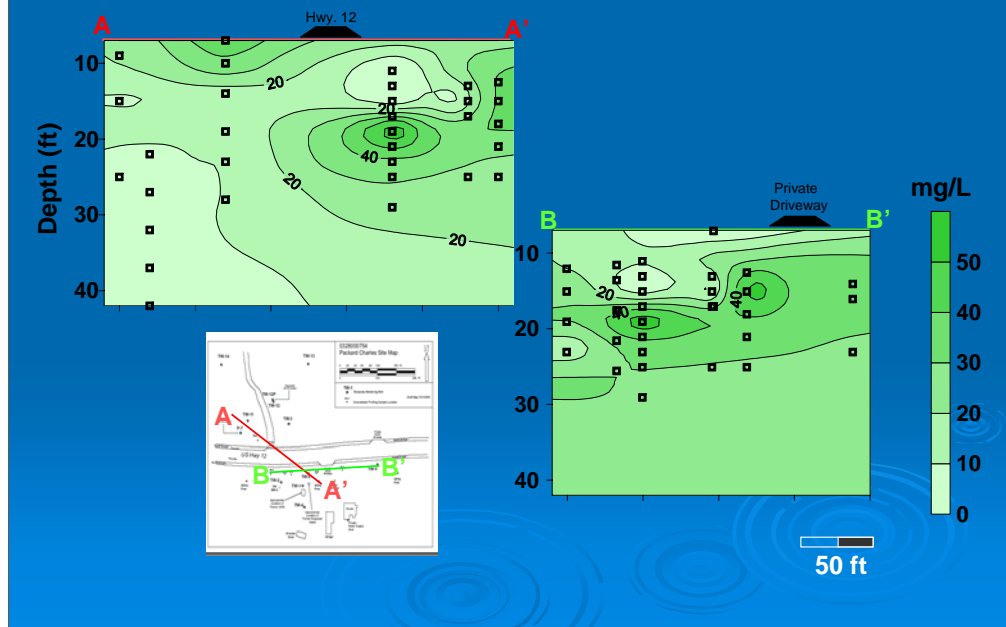
- Because biodegradation of many petroleum hydrocarbons, particularly benzene generally occur under iron reducing conditions coincidental zones of high benzene and ferrous iron suggest that chemical reduction is taking place
- Ferrous iron was observed where contaminant levels were highest. Lower values coincide with the high dissolved oxygen concentrations along the north side of the road, and are consistent with a lack of chemical reduction in these areas.

Manganese



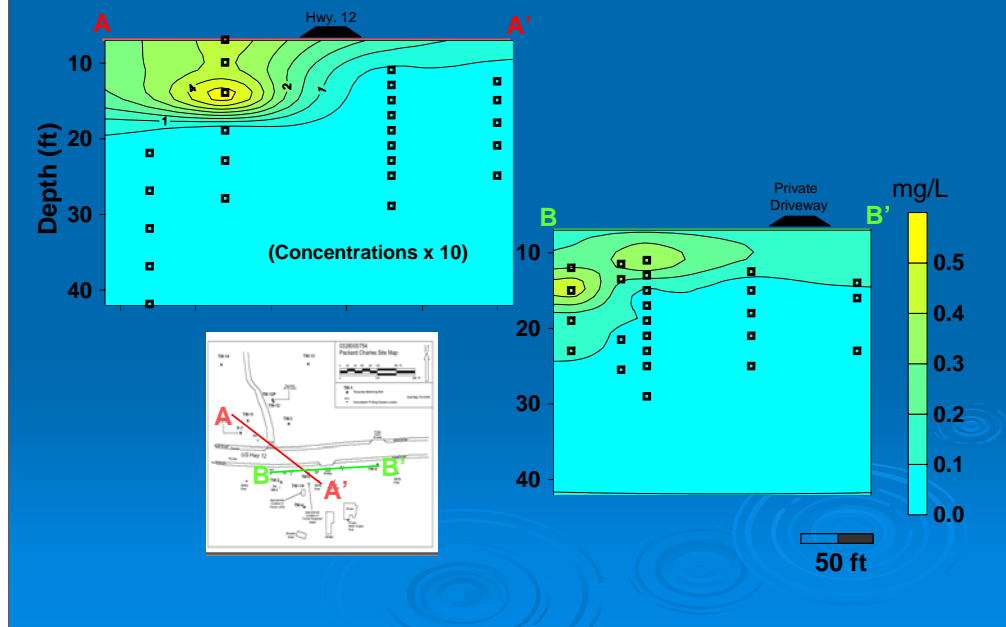
- Dissolved manganese concentrations are low in the immediate source area, and are highest adjacent to the source area.
- Don't overlap with source as Fe did.
- Possible explanation - fill of varied composition.

Sulfate



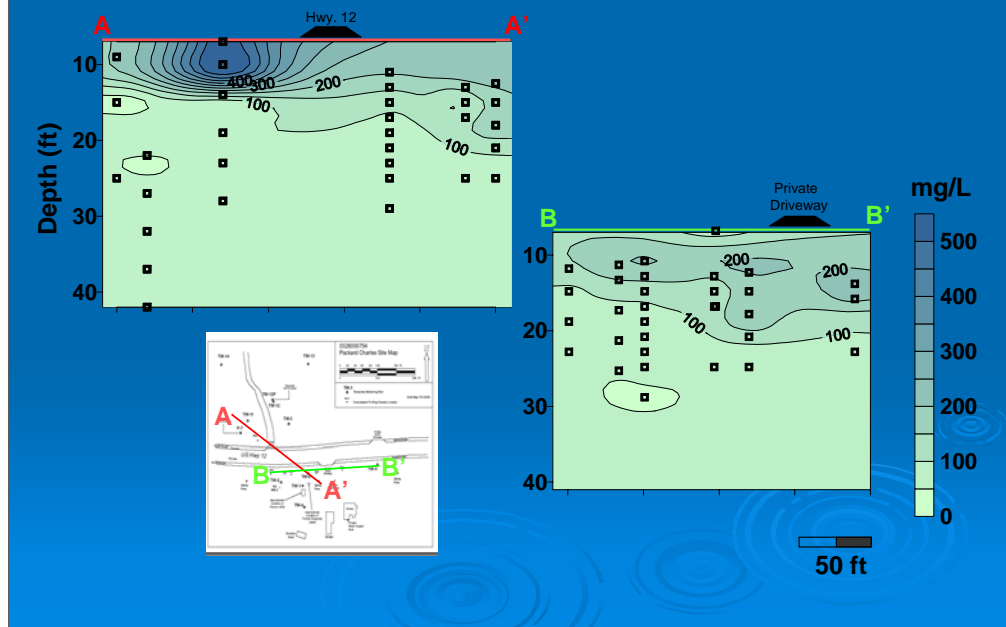
- Sulfate concentrations are similar to Fe in that they are also lowest in the the contaminated zone
- High where DO and Fe and Mn are high.
- The lack of SO₄ in the contaminated zone suggests the presence of sulfate reducing conditions.
- (HS gas was observed in the field, but not quantified in many of the samples.)
- The iron, manganese, and sulfate profiles strongly suggest the presence of chemical reaction processes that are typical of natural attenuation sites.

Dissolved Oxygen



- Natural attenuation indicators suggest suitable conditions for natural attenuation of benzene
- Dissolved oxygen is low throughout the site except for immediately north of the road.
- The high DO zone is coincident with areas where coarser sediments are near land surface and storm water is diverted away from the road. The high DO may indicate infiltration of recent storm runoff

Chloride



- To assess the role of vertical recharge we investigated also monitored Na and Cl associated with road salt. Cl is shown here.
- Cl concentrations are highest adjacent to highway 12 and with depth on the the south side of the road.
- The deeper Cl is consistent with infiltration of historical road salt applications on the south side of the road (near driveway).
- Given the presence of DO and the sharp Cl front on the north side of the site, the Cl on the north side appears to be relatively recent.

Conclusions

- Zones of low dissolved oxygen and sulfate, and high iron and manganese coincide with ground-water contamination suggesting natural attenuation.
- A stable contaminant plume appears to be maintained by residual soil contamination, and limited to the near-source area by natural attenuation processes.
- Recent highway modifications may have altered the local flow direction and influenced the contaminant distribution and ground-water chemistry.
- Future site investigations will benefit from high-resolution field screening for natural attenuation processes.

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